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Grain growth from amorphous phase

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Time dependence of the grain growth in phosphorus doped silicon thin films deposited in situ at 530 °C was investigated. The samples were annealed at 950 °C in different time intervals. The theories, which give the t^n time dependent increase of grain size, cannot fit the observed data. We derived a differential equation which describes the grain growth from amorphous phase. Our experimental results and the solution of the differential equation show the effect of grain growth stagnation and even grain growth stop. The solution also comprises all the features of the result of the Monte Carlo simulation of the grain growth of pure materials. [http://dx.doi.org/10.1063/1.4870242]

Recently published Monte Carlo (MC) simulation study showed stagnation and even stopping of the crystal growth even in high purity materials.[1] We present an analytical solution for the grain growth based on the differential equation derived for the grain growth from amorphous phase. Interestingly enough, besides the solution describes well our experimental data, it shows essential features as afore mentioned MC computer simulation.

Properties of polycrystalline silicon are highly dependable on its structural composition: grain size, its geometry together with the grain boundary content. In many cases, grain size determines today's application but also it will be important in some future applications. Large grained material is preferred in the photovoltaic energy conversion. On the other hand, in the field of thermoelectrics, an expected and desired future application, smaller grains result in stronger phonon scattering which leads to a better figure of merit.[2] An aggressive device scaling present nowadays results in increased sensibility of such devices on polycrystalline silicon grain stability and dopant concentration. Due to increased interest in nanoscience and its applications, stability of polycrystalline materials is one of the important topics of the solid state physics today, either experimental or theoretical.[1–3] Grain size control is an important task in optimizing material properties. One essential aspect of this problem is to understand the grain growth stagnation mechanism. Moreover and in addition, as seems to us, there is not achieved an answer on the question what is the final state of the grain growth: monocrystalline or polycrystalline state.

Experiments on the time dependence grain growth are important because they can reveal the underlying physics which governs the grain boundary migration and can also reveal the grain growth stagnation mechanism.[4]

One expects:

$$\langle a \rangle \propto t \tag{1}$$

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in the case of the strain stored energy introduced for example by cold-work. In this equation, t is time and $\langle a \rangle$ is an averaged linear grain dimension. The linear dependence in t is obtained also in the case where the triple junction mobility is responsible for the grain growth.[3]

Interface energy induces growth in the form:[4]

$$\langle a \rangle \propto t^{1/2} \tag{2}$$

If the grain boundaries are dragged by impurities or small inclusions, grain growth is described by:

$$\langle a \rangle \propto t^{1/3} \tag{3}$$

A deeper insight into the grain growth one can get from a simple kinetic equation:[5]

$$\frac{da}{dt} = k\left(\frac{1}{a*} - \frac{1}{a}\right) \tag{4}$$

This equation can describe the grain growth by moving the grain boundaries caused by their geometry curvature). At a certain point in time t, if a particular grain with size a is smaller than the average sized grain a*, the grain will lose its volume and shrink (Eq. (4) is negative). If $a > a$*, the grain will grow on the account of smaller grains.

Solutions of Eq. (4) are similar to relations (1)–(3):[6]

$$\text{in 2D case} : \langle a \rangle \propto t^{1/3} \tag{5}$$

$$\text{in 3D case} : \langle a \rangle \propto t^{1/4} \tag{6}$$

All these solutions for $t \to \infty$ give $a \to \infty$, indicates that the final state of the grain growth process is a monocrystalline state. This is in accordance with the theory which states that the thermodynamic equilibrium state of crystalline material is a single crystal. However, in polycrystalline material, grain growth rate decreases and finally grains to grow at some averaged grain size. This is an important result of Ref. 1.

Various stagnation mechanisms were proposed to explain the existence of, in fact, metastable polycrystalline state. A short review on this subject was given in Science,[1] where the authors proposed an additional growth stagnation mechanism that caused by the grain surface roughness. The Monte Carlo simulations show that even in the case of very smooth grains the final state of the grain growth is a polycrystalline state.

Precise analysis of our data of the grain growth in doped silicon thin films, where the grain grow starts from the amorphous phase, shows the grain growth stagnation. Interesting is that the solution of the differential equation, which we derived for the grain growth from amorphous phase, can describe also the grain growth in the case of very pure materials as well as our experimental data.

Thin silicon films were deposited on the <100> p-type single crystalline Si wafers in the LPCVD (low pressure chemical vapor deposition) reactor. In situ doping was achieved by parallel flows of silane and phosphine at 530 °C. Working conditions in the reactor resulted in the same thicknesses (230 nm). Dopant, phosphorus, concentrations of $2 \cdot 10^{20}$ cm^{-3} for all the samples was determined by SIMS (secondary ion mass spectrometer). Electrical activation was achieved through crystallization in the process of RTA (rapid thermal anneal) at 950°C. RTA was performed by the high power IR (infra red) lamps as heat sources instead of conventional annealing because a better time control for the short term annealing can be achieved together with high heating and cooling rates.

The initially amorphous sample shows crystallization already after 10 s. Fig. 1 shows XRD (x-ray diffraction) of the sample before annealing (inset) and after annealing. The difference in structure is evident – absence of the characteristic XRD peaks indicates the amorphous structure.

The polycrystalline structure of the same sample can also be observed from the SEM image (scanning electron microscope) in Fig. 2. For comparison, Fig. 3 shows the micrograph of the surface morphology belonging to the sample deposited as polycrystalline at 580 °C and subsequently annealed for 10 s at 950 °C. One can notice that grain sizes and shapes of these two samples are

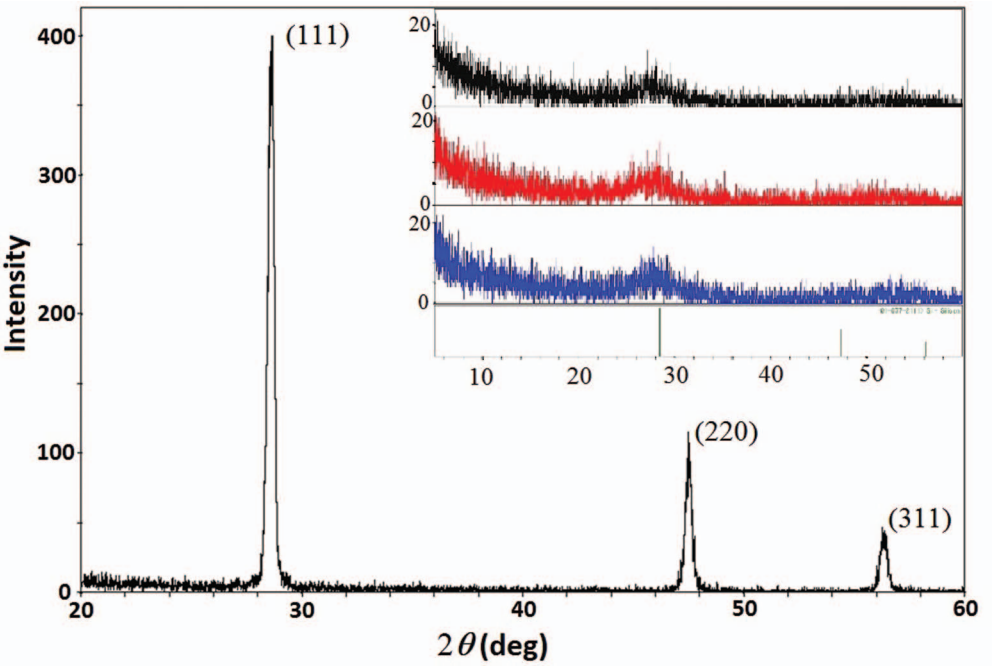

FIG. 1. XRD of the sample annealed for 10 s at 950 °C (T_{DEP} = 530 °C) taken at $\omega = 0.3°$. In the inset: XRD of the same sample before the annealing process.

markedly/essentially different. Initially amorphous samples (Fig. 2) have larger grains which have rather smooth surfaces and because of that it is not easy to precisely differentiate the grains without special software tools.

For the grain size measurements an Image tool was used. The grains are approximated by ellipses each covering a silhouette visible on the micrograph. Average grain size is calculated taking into account both the major and minor axes lengths. Initially polycrystalline samples have grains with diameters of about 100 nm which sizes do not change after 10 s annealing (Fig. 3). Data obtained for the samples deposited as amorphous show that grain size increases with the annealing duration. Our overall results are in a good agreement with the ones published by Kamins[7] who states that the samples initially deposited as amorphous and then annealed will have larger grains and smother surface than the ones initially deposited as polycrystalline and annealed at the same temperature. Larger grains are the result of lower density of nucleation sites than in the initially polycrystalline material, created mainly at the interface between substrate and the deposited amorphous layer. In the crystallization process, grains form starting from the nuclei and grow on the account of the amorphous content. In the initially polycrystalline material, the nuclei concentration is much more dense meaning that the area for the grain growth is constrained and that results in smaller grains.

In Fig. 4, the mean grain sizes, a, of the initially amorphous samples are plotted as a function of the annealing duration, t (circles). Dashed lines represent the theoretical curves according to Eqs. (2), (3), and (5). However, the data obtained in the presented work cannot be fitted well by these theories. To explain such behaviour, it is assumed that grains grow on the account of the amorphous phase. In that sense, Eq. (4) can be transformed into:

$$\frac{da}{dt} = k\left(\frac{1}{a^*} - Aa\right) \tag{7}$$

We take that all the grains grow on account amorphous phase. Hence, the bracket is positive and we can put in (7) $1/a$ instead $1/a^*$. The rate of change of the grain size, da/dt, decreases as grain size increases. This is described by the first term: $1/a$. At the same time, the rate of growth decreases in time as the amorphous volume fraction reduces, or analogously, when the content of crystalline content increases. This is described by the term $-Aka$. Grain stops to grow when the term in the

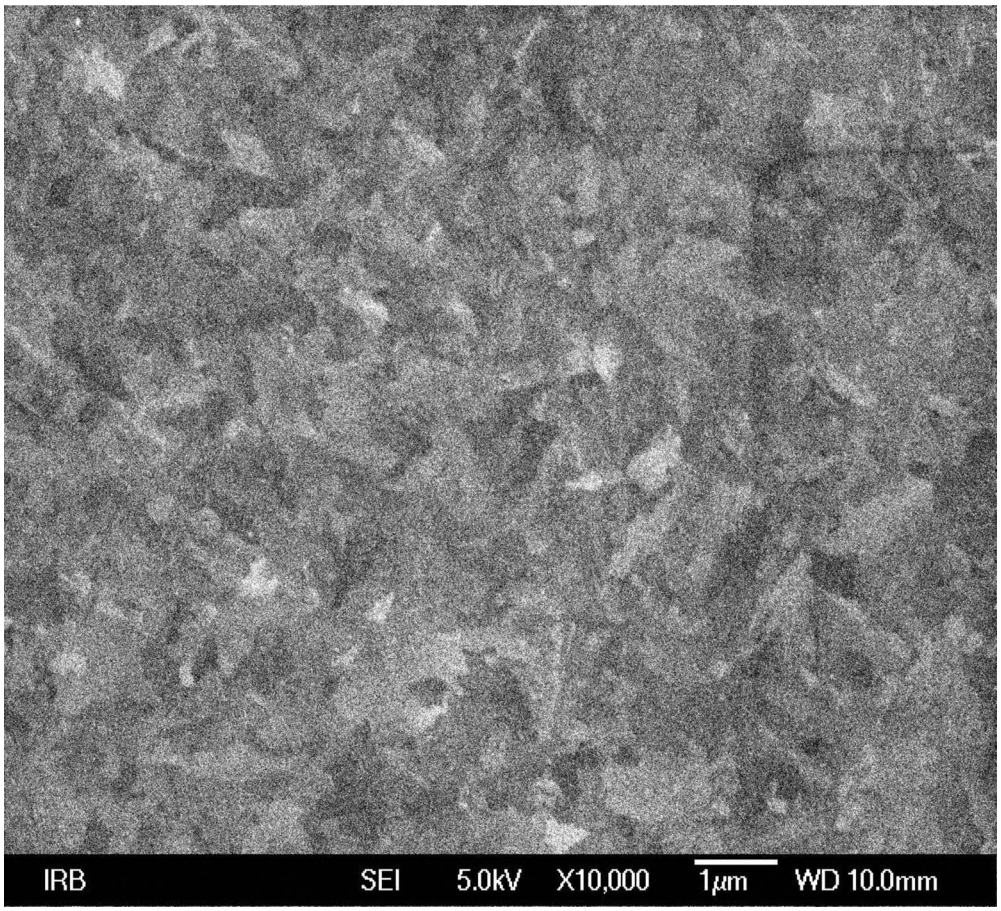

FIG. 2. SEM image of sample deposited as amorphous and RTA annealed for 10 s at 950 °C.

brackets becomes zero; this means, when the amorphous content is vanished. Thus one can infer the expression for the constant A:

$$A = 1/a_M^2 \tag{8}$$

Solution of differential equation (7) is:

$$a(t) = \sqrt{\frac{1}{A}\left[1 - \exp(-2kAt)\right]} \tag{9}$$

Or in the terms of Eq. (8):

$$a(t) = a_{\mathrm{M}}\sqrt{1 - \exp(-2kt/a_{\mathrm{M}}^2)} \tag{10}$$

These expressions refer to the average value of a. Our experimental data can be fitted with:

$a_{\mathrm{M}} = 526$ nm and $2kA = 0.047\ \mathrm{s}^{-1}$ (full curve in Fig. 4). The initial slope of the curve is: $(2k)^{1/2} = 114\ \mathrm{nms}^{-1/2}$. One can define a characteristic time: $\tau = 1/2kA = 21.27$ s. At this moment, the average grain size is: $a \approx 0.8a_{\mathrm{M}}$.

The solution (9)/(10) shows three basic features:

(i) for $t \to \infty$, $a \to a_{\mathrm{M}}$, meaning that the grain growth stagnation and even the grain growth stop are included into Eq. (4);

(ii) for $t \to 0$, $a \to (2kt)^{1/2}$, meaning that at the beginning the rate of growth is higher if the grain is smaller. The grain growth is determined only by the first term of Eq. (7): $\mathrm{d}a/\mathrm{d}t \sim 1/a$. Such dependence is expected when the interface energy governs the grain growth. In this case, the energy is higher at the boundaries which are more bended, i.e., when a grain is smaller.

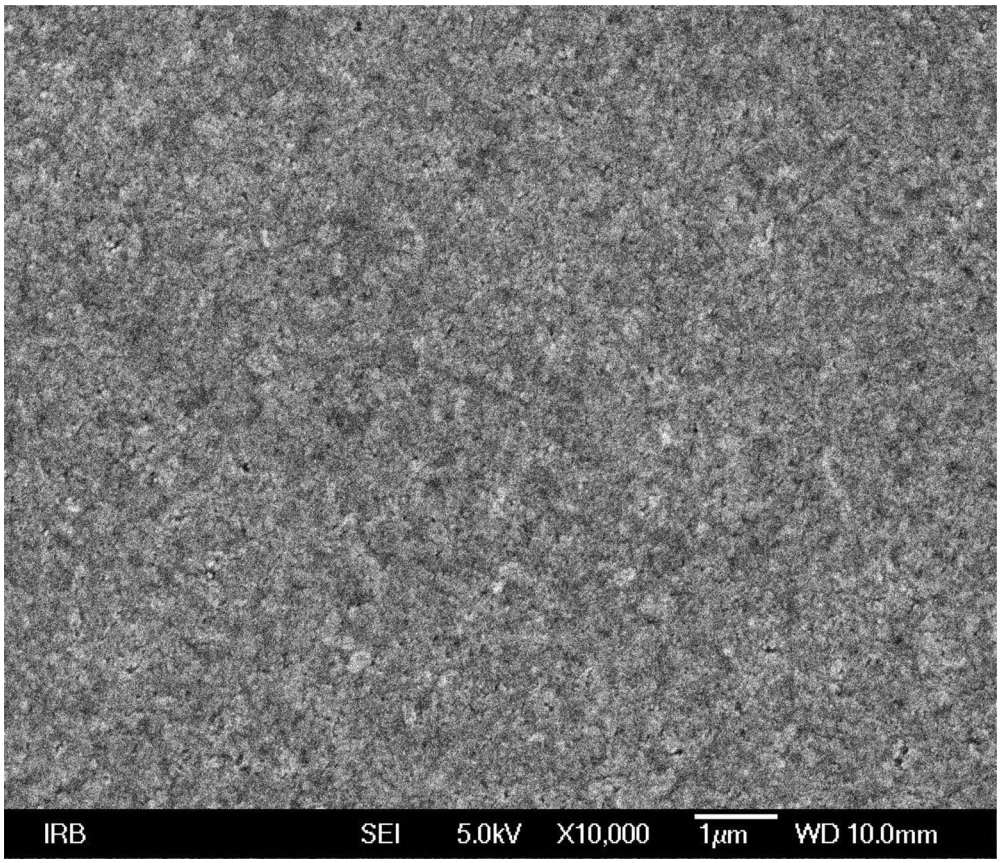

FIG. 3. SEM image of sample deposited as polycrystalline and then RTA annealed for 10 s at 950 °C

(iii) the term $-kA \cdot a$ in Eq. (7) gives the exponential saturation in Eq. (9)/(10) leading to grain growth stop.

To summarize: Eq. (7) describes grain growth which is governed by interface energy (*ii*). The growth of a grain is accompanied with processes of moving atoms in amorphous matrix onto the proper positions forming crystallites. It happens more likely at the border of already present nuclei because there are energetically favorite places. The rate of these processes is characterized by the proportionality constant k (the first term in Eq. (7)). It is interesting to note that the stagnation and finally grain growth stop (the second term in Eq. (7)) is also proportional to k. This is clear because by the rapidness of the grain growth the content of amorphous phase decreases (*iii*). The grains spread to the areas where the amorphous phase still exists. This can explain very diverse grain shapes. The grain growth from amorphous phase will stop when the amorphous volume fraction vanishes (*i*).

We should answer whether the grains do grow on account of amorphous content or on account another grains. It is already mentioned and discussed the great differences of the sizes and shapes of the grains in the films deposited as crystalline and the samples deposited as amorphous. Another evidence of the grain growth on account of amorphous phase is resistivity measurement.[8] With increasing duration of annealing, the resistivity of the samples decreases. This means that current carrier concentration (number of current carriers per sample volume) increases. As the activations of current carriers happen in crystal, it follows that the crystalline content increases on account of amorphous content. In Ref. 8, we show that the phosphorus concentration of $2 \cdot 10^{20}$ cm^{-3} is almost all soluble at 950 °C.

It is worth to note that the solution, Eq. (10), comprises all three features (*i–iii*) of the result obtained by the Monte Carlo simulations for the grain growth in the case of pure metals.[1] The data from figure 3 of Ref. 1 are fitted to our theoretical result are presented in Fig. 5. In the table in the

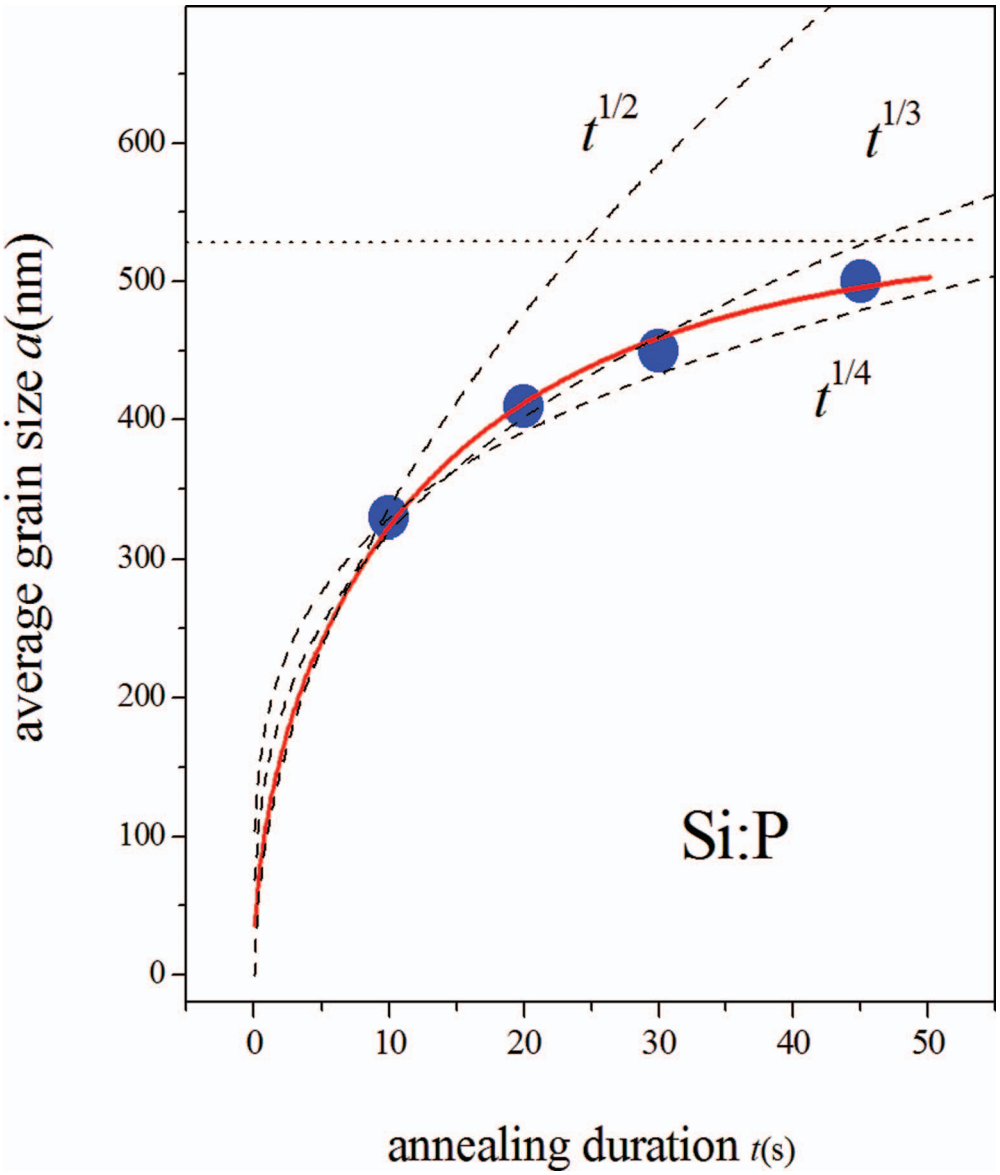

FIG. 4. Mean grain size value a of the samples deposited as amorphous as a function of the annealing duration t (circles). Dashed lines represent the fits to the experimental data by Eqs (2), (3), and (5). Full line is the fit according to Eq. (6).

figure, the values of the parameters derived from the simulated data and our theory are compared. The discrepancies between the theory and published results in Ref. 1 are negligible; precisely, in average, 4%.

Certainly, the question is whether or why the differential equation derived for the grain growth from the amorphous phase, Eq. (7), is appropriate to describe the grain growth in the case of very pure polycrystalline materials. The first term of Eq. (7) has the same physical origin in both cases, as is discussed afore. The stagnation and finally the stopping of the grain growh in the case of the systems considered in Ref. 1 is ascribed to the grain surface roughness.[1] We note that effects roughness is certainly larger if a grain is larger and, hence, the second term in Eq. (7) could describe the effect of roughness. In a better and more realistic description of an underlying physics, this term could be replaced with an appropriate term. But, as Fig. 5 shows, in the case of the grain growth of pure materials, the solution of Eq. (7), i.e., Eq. (10) describes rather well the experimental data.

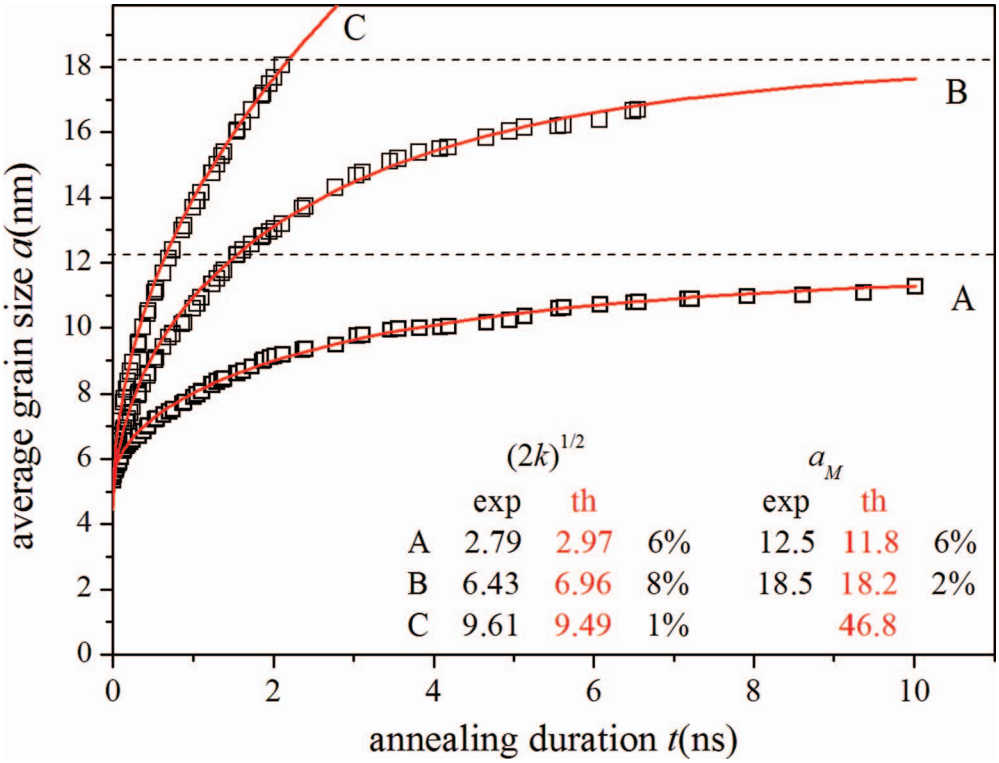

FIG. 5. Comparison between the theory (red line) and the date obtained by computer simulation (squares) taken from Ref. 1. In the table, it is compared: a) the initial slope of the experimental curve (black), i.e., $(2k)^{1/2}$ (Fig. 3 in Ref. 1) and the same quantity from the fitting curve (red); b) the a_M from the experimental data (Fig. 3 in Ref. 1) and the fitting parameter a_M (red). For sample C, Eq. (10) predicts a_M by fitting the data of earlier stage of annealing.

In conclusion, we may say that we have derived a new differential equation, Eq. (7), for the grain growth. Its solution can describe the stagnation and even the stop of the grain growth unlike solution of an earlier differential equation, Eq. (4). Although Eq. (7) is derived for the case of the grain growth from amorphous phase, we show that the solution can fit the data of some other cases. For example, the results of the grain growth in the case of pure metals obtained by the Monte Carlo simulation are shown in Fig. 5.[1] Having an analytical solution to describe a physical process instead a computer simulation is certainly useful. It enables comparison and systematization of various experiments. Also, it enables to predict the final grain size in an early stage of annealing.

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